



Recovery of high purity precious metals from printed circuit boards

Young Jun Park*, Derek J. Fray

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, United Kingdom

ARTICLE INFO

Article history:

Received 28 July 2008

Received in revised form 5 September 2008

Accepted 5 September 2008

Available online 21 September 2008

Keywords:

Printed circuit board

Recovery

Gold

Silver

Palladium

ABSTRACT

Waste printed circuit boards (WPCB) have an inherent value because of the precious metal content. For an effective recycling of WPCB, it is essential to recover the precious metals. This paper reports a promising method to recover the precious metals. Aqua regia was used as a leachant and the ratio between metals and leachant was fixed at 1/20 (g/ml). Silver is relatively stable so the amount of about 98 wt.% of the input was recovered without an additional treatment. Palladium formed a red precipitate during dissolution, which were consisted of $\text{Pd}(\text{NH}_4)_2\text{Cl}_6$. The amount precipitated was 93 wt.% of the input palladium. A liquid–liquid extraction with toluene was used to extract gold selectively. Also, dodecanethiol and sodium borohydride solution were added to make gold nanoparticles. Gold of about 97 wt.% of the input was recovered as nanoparticles which was identified with a high-resolution transmission electron microscopy through selected area electron diffraction and nearest-neighbor lattice spacing.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

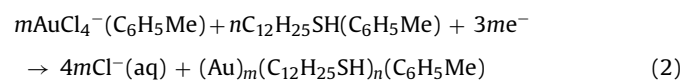
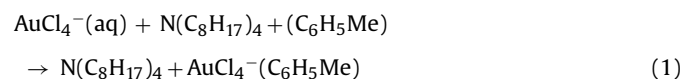
Electrical and electronic equipments (EEEs) have developed rapidly and their average lifespans have reduced due to the changes in functions and designs. This tendency caused large amount of the waste and recently became a serious environmental problem. In case of the European Union, waste electrical and electronic equipment (WEEE) directives were established and have encouraged WEEE to be treated in an environmentally efficient way [1,2]. However, the treatments are still relying on simple methods such as incinerator and landfill.

Printed circuit board (PCB) is a key component in the WEEE. PCB assemblies typically have the composition as shown in Table 1, which consists of various metals including precious metals such as gold, silver and palladium [3]. The best option in a waste treatment is recycling. There have been several studies on the recycling of materials by mechanical [4,5], thermal [6] and chemical [7,8] processes, but most of them dealt with recovery of one or two specified materials of all PCB compositions. Recently, Pilone and Kelsall [9] reported on multi-metal electrodeposition with a mathematical model.

Our research aims at development of a new process which can recover high-purity metals from a PCB waste. The steps of the process steps are indicated in Fig. 1. Firstly, iron and aluminium are separated by magnetic and eddy current, respectively. Solder recov-

ery was reported in our previous paper [10]. A technology for copper separation is well established through ammonium sulphate leaching, solvent extraction, and electrowinning [11]. The last two steps are about recovery of precious metals and separation of nickel and zinc.

Precious metals in PCB account for more than 80% of the total intrinsic value even though the amount is less than 1 wt.%. This paper suggests a promising method for the precious metals recovery. Aqua regia was selected as a leachant and the target materials were silver, palladium, and gold. As shown in Table 1, gold is the most important material in PCB recovery. In this research, gold was recovered as nanoparticles to improve the value. The overall reaction related to formation of gold nanoparticles is summarized in the following equations [12]:



2. Experimental

2.1. Dissolution of metals

This research is on the recovery of precious metals following the copper removal in Fig. 1. Metal mixtures of 5 g were prepared as the

* Corresponding author. Tel.: +44 1223 334315; fax: +44 1223 334567.

E-mail addresses: yjp21@cam.ac.uk (Y.J. Park), djf25@cam.ac.uk (D.J. Fray).

Table 1
Compositions and the intrinsic values of PCB metals [3].

Component	Wt.%	Value ^a (£/kg)	Intrinsic value of PCB	
			(£/kg of PCB)	(%)
Gold	0.025	14200.00	3.55	65.4
Palladium	0.010	6200.00	0.62	11.4
Silver	0.100	250.00	0.25	4.6
Copper	16.0	3.30	0.53	9.7
Aluminium	5.0	1.20	0.06	1.1
Iron	5.0	0.10	0.01	0.1
Tin	3.0	8.10	0.24	4.5
Lead	2.0	1.30	0.03	0.5
Nickel	1.0	13.20	0.13	2.4
Zinc	1.0	1.20	0.01	0.2

^a Metal values are based on December 2007 London Metal Exchange (LME) levels.

ratio of Table 1 (2.342 g Zn, 2.342 g Ni, 0.234 g Ag, 0.059 g Au and 0.023 g Pd). All metals were 0.5-mm diameter wires with purity of more than 99.9 wt.% to make the surface areas proportional to the weights. In order to find out the effect of the ratio between metals and leachant, aqua regia solutions of 50, 100 and 200 ml were freshly prepared before each experiment by mixing ACS reagent grade concentrated hydrochloric and nitric acids. The dissolution was indicated by a percentage of dissolution:

$$\% \text{ of dissolution} = \frac{\text{dissolved amount in the solution (g)}}{\text{input amount (g)}} \times 100 \quad (3)$$

The prepared aqua regia was poured to metal wires in Duran erlenmeyer flasks (300 ml) covered with a watch-glass and remained stationary at $20 \pm 2^\circ\text{C}$. The concentrations according to time were analyzed by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES, VARIAN LIBERTY-AX).

2.2. Silver and palladium separation

Silver is relatively stable in aqua regia so it remained unreacted during reactions. Palladium formed a red precipitate on the bottom of flasks. Therefore, these were separated by a physical screening after a gravitational settling of 3 h before gold extraction processes. The precipitates, including the remaining silver wire and red powders, were investigated by a scanning electron microscopy (SEM, JEOL-5800LV) with energy dispersive spectroscopy (EDS), an X-ray photoelectron spectroscopy (XPS, VG Scientifics-ESCALAB 250) and an X-ray diffractometer (XRD, Bruker AXS D8). For the XRD analysis on the surface of the silver wire, the layer formed on the surface was removed from the body and then analyzed in the status of particles.

2.3. Gold extraction and synthesis of the nanopowders

The leachant after removal of precipitates was diluted 2.5 times with deionized water to achieve an effective gold extraction. Toluene with ACS reagent grade was used as an extractant and tetraoctylammonium bromide with HPLC grade was added to toluene as a phase-transfer reagent (10 mM in toluene). The ratio between an organic extractant (OE) and an aqueous solution (AS) may have an influence on the selective extraction of gold so the leachant (100 ml) were mixed with the extractant of 50, 100 and 200 ml, respectively. The two-phase mixtures were stirred at 400 rpm for 10 min and then dodecanethiol (50 mg) was added to the organic phase. A freshly prepared sodium borohydride solution was also added very slowly to the organic phase in order to prevent metal ions in the aqueous solution from being reduced. A metal

distribution coefficient (D) was employed to evaluate the selective gold extraction and was calculated in the following equation:

$$D_i = \frac{M_{OEi}}{M_{ASi}} \quad (4)$$

where M_{OEi} and M_{ASi} represent the amount of metal i that has equilibrated in the organic extractant and the aqueous solution. After additional stirring for 2 h, the organic extractant, toluene, was separated, evaporated up to 10 ml in a rotary evaporator and was mixed with 250 ml ethanol to remove excess thiol. The mixture was kept for 5 h at -20°C and the dark brown precipitates generated on the bottom were filtered and washed again with ethanol. After drying in the evaporator, the product was observed using a high-resolution transmission electron microscopy (HR-TEM, JEOL-4000FX). In addition, the composition was identified with selected area electron diffraction (SAED), nearest-neighbor lattice spacing, and EDS.

3. Results and discussion

3.1. Dissolution of PCB metals in aqua regia

One of major factors which could have an influence on dissolution of metals is a relative amount between metals and leachant. First of all, a dissolution tendency was investigated with the metals/leachant ratio of 1/10, 1/20 and 1/40 (g/ml).

Fig. 2 shows the dissolution of metals in aqua regia according to time. Zinc reacted vigorously so it was dissolved completely within several seconds regardless of the ratios. In case of the ratio of 1/10, the amount of leachant was not sufficient to dissolve the metals so a lot of precipitate with various colours and sizes were generated. As the ratio changed to 1/20 and 1/40, the small red powders were only precipitated around an unreacted silver wire. Nickel dissolved completely in the ratio of 1/20 and 1/40 in 3 h (Fig. 2(a)). Gold showed about 97% and 100% dissolution in the ratio of 1/20 and 1/40, respectively, whilst it dissolved about 80% in the 1/10 ratio (Fig. 2(b)). On the other hand, the solubility in silver and palladium was very low as shown in Fig. 2(c) and (d). As the ratio changed from 1/10 to 1/40, the dissolution of silver increased from 0.8% to 7.2%. Palladium showed a unique reaction with aqua regia, which made red precipitates around the palladium wire and dissolved completely within 3 h. However, the detected amount of palladium in aqua regia was just between 5.4% and 7.8% of the input in the ratio of 1/20 and 1/40, respectively.

In this research, the optimum dissolution conditions were determined and fixed at the metals/leachant ratio of 1/20 (g/ml) and the dissolution time of 3 h in consideration of a high gold solubility and a low silver and palladium dissolution.

3.2. Separation of silver and the surface change in aqua regia

Generally, aqua regia dissolves most of metals. But, silver has a strong chemical durability to aqua regia [11]. On the dissolution experiments, the colour of the silver wire turned black but the shape still remained the same. A SEM micrograph in Fig. 3 shows that the layer formed on the surface of silver wire and the thickness is about $20 \mu\text{m}$. The XRD analysis in Fig. 4 shows that the black surface consists of AgCl. Small peaks from Ag were also detected, which might come from the body of the silver wire when the black surface was removed. This AgCl layer could play an important role to prevent silver from dissolving in aqua regia. The silver with a AgCl layer can be recovered to pure silver by conventional purification processes [11].

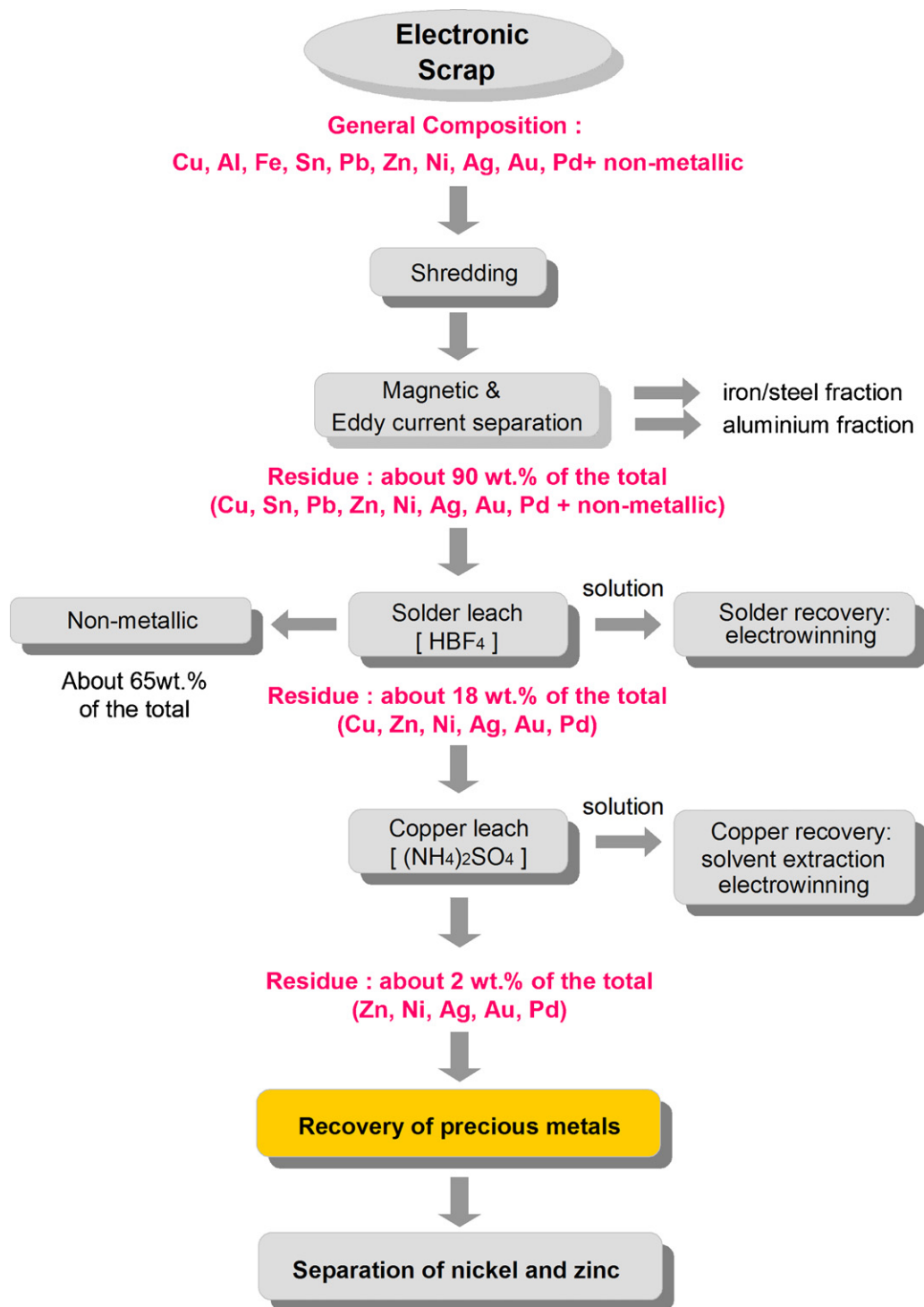


Fig. 1. A new recycling process of PCB metals.

3.3. Precipitation of a palladium complex

The results in Fig. 2(d) indicate that the precipitates on the dissolution reaction could include palladium complexes. From a SEM-EDS analysis, it was found that the precipitates mainly consist of a palladium-chlorine complex with a cubic structure and the relative ratio of palladium to chlorine is about 33–67 by weight (Fig. 5). The results of XRD and XPS matched exactly with those of $\text{Pd}(\text{NH}_4)_2\text{Cl}_6$ (Fig. 6). The fraction of $\text{Pd}(\text{NH}_4)_2\text{Cl}_6$ particles in the

precipitates was about 99% from an XRD quantitative analysis and the precipitates could be also recovered to pure palladium through conventional refining processes [11].

In order to identify the formation of $\text{Pd}(\text{NH}_4)_2\text{Cl}_6$, the zinc, nickel, gold and silver wires were dissolved in a separated aqua regia, respectively. The aqua regia solutions containing just one metal ion were mixed with one another. However, all combinations among the aqua regia solutions did not cause any precipitation, which means that the precipitates were formed on the process of

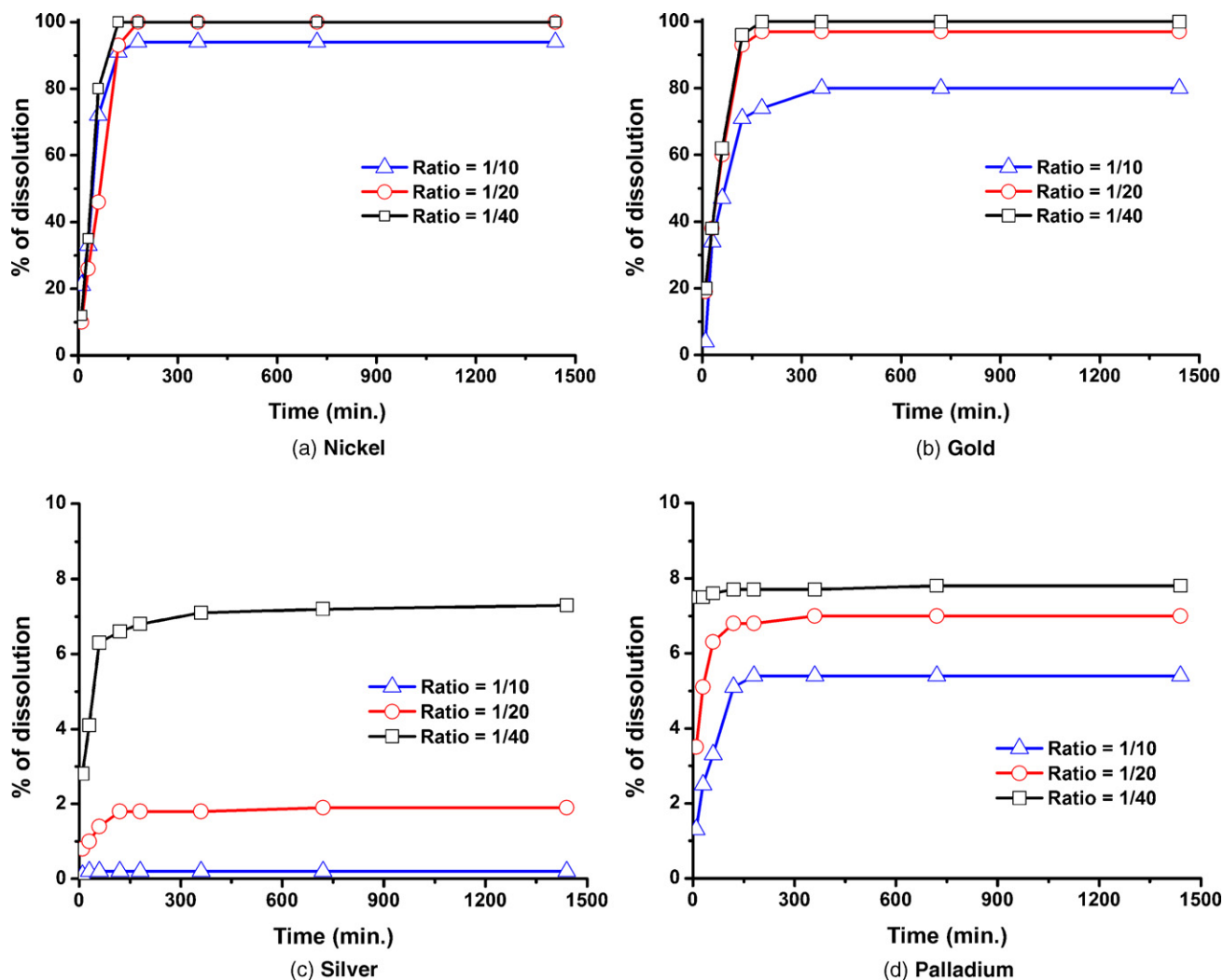


Fig. 2. Dissolution of PCB metals in aqua regia according to time. Ratios of 1/10, 1/20, and 1/40 note that PCB metals of 5 g reacted with aqua regia of 50, 100, and 200 ml, respectively. % of dissolution indicates a relative amount in Eq. (3). Other metals except zinc were shown in (a) nickel, (b) gold, (c) silver, and (d) palladium. Plotting of zinc is meaningless because it happens in a few seconds.

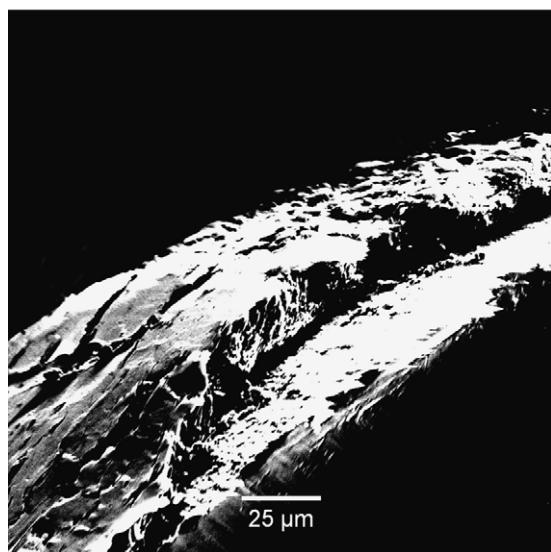


Fig. 3. SEM micrograph of the profile of the silver wire surface after contacting with aqua regia for 3 h. The EDS analysis showed that the layer formed on the surface consisted of silver and chlorine.

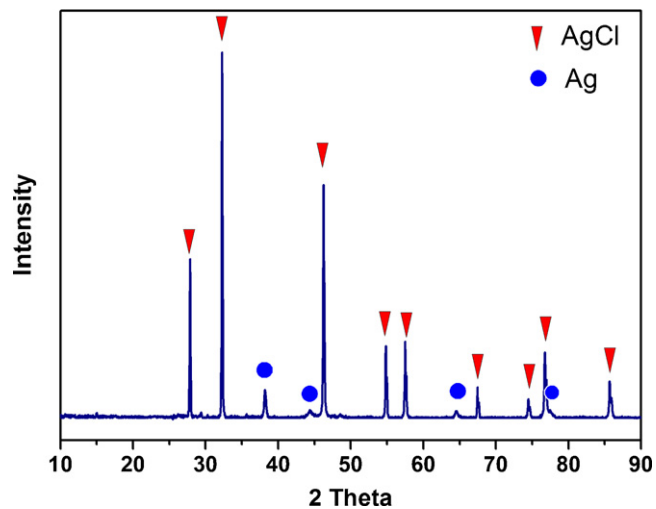


Fig. 4. X-ray diffractogram of the surface of silver wire after contacting with aqua regia.

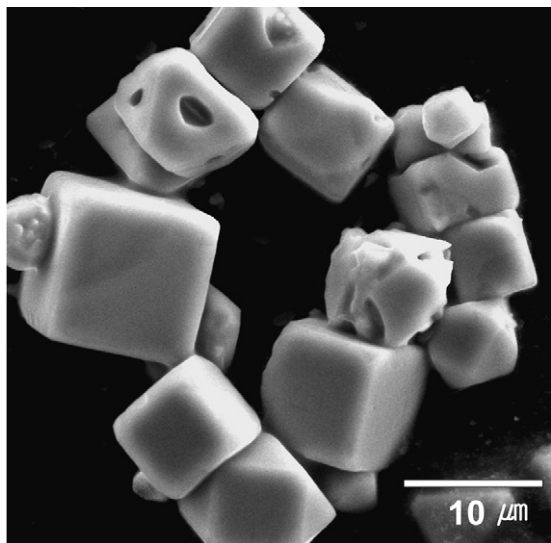


Fig. 5. SEM micrograph of the red precipitates.

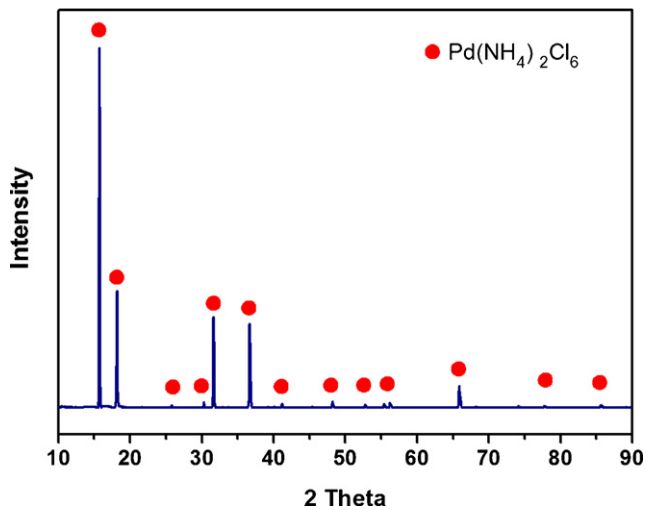


Fig. 6. X-ray diffractogram of the red precipitates.

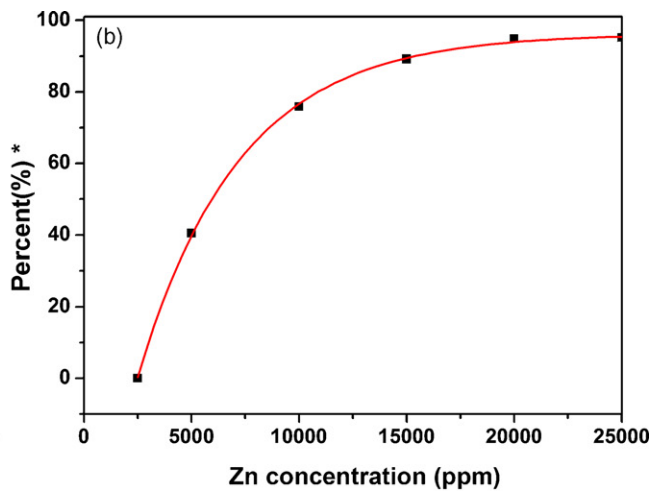
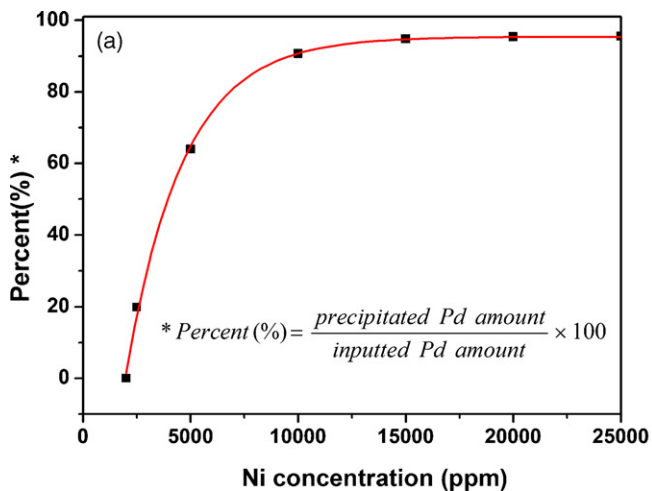


Fig. 7. Changes in the palladium precipitation according to the concentration of (a) nickel and (b) zinc. The vertical axis represents a percentage of palladium precipitation as indicated.

Table 2

Metal distribution coefficients (D_i) according to the ratio between aqueous solution and organic extractant.

Component (i)	D-value		
	2:1 ^a	1:1 ^a	1:2 ^a
Zinc	0.001	0.001	0.002
Nickel	N.E. ^b	N.E.	N.E.
Silver	N.E.	N.E.	N.E.
Gold	83.545	231.500	237.462
Palladium	N.E.	N.E.	0.015

^a Aqueous solution:organic extractant (v/v).

^b Not extracted ($D < 0.0005$).

the dissolution of metals. When a palladium wire was put into aqua regia with the zinc or the nickel ions, red powders were precipitated and identified as $\text{Pd}(\text{NH}_4)_2\text{Cl}_6$. The formation of the precipitates must be related to a concentration of metal ions because there was no precipitate when only palladium without other metals was dissolved in aqua regia. Therefore, the relationship between precipitation and concentration of zinc and nickel was investigated as shown in Fig. 7. The precipitation started from around 2500 ppm and was saturated at about 15,000 and 20,000 ppm of nickel and zinc ions, respectively. When aqua regia is poured into PCB metals, the concentration of zinc reaches up to more than 20,000 ppm within several seconds whilst those of other metals are low. This indicates that the concentration of zinc could play a key role in the precipitation of palladium. Therefore, the formation could be summarized as follows:

- (1) Zinc is dissolved into aqua regia in several seconds and makes an environment for palladium precipitates.
- (2) Palladium dissolves and forms PdCl_6^{2-} ions in aqua regia [13].
- (3) At the same time, palladium reduces NOCl or HNO_3 to NH_4^+ on the surface of the wire [13,14].
- (4) The reaction between PdCl_6^{2-} and NH_4^+ forms $\text{Pd}(\text{NH}_4)_2\text{Cl}_6$.

3.4. Gold extraction and synthesis of the nanoparticles

Toluene can extract gold selectively. There were several papers which reported the efficiency of a selective gold extraction according to chlorine concentration. They showed that high concentration of chlorine hinders a selective extraction of gold [15,16]. Accordingly, aqua regia in the experiment was diluted 2.5 times with deionized water.

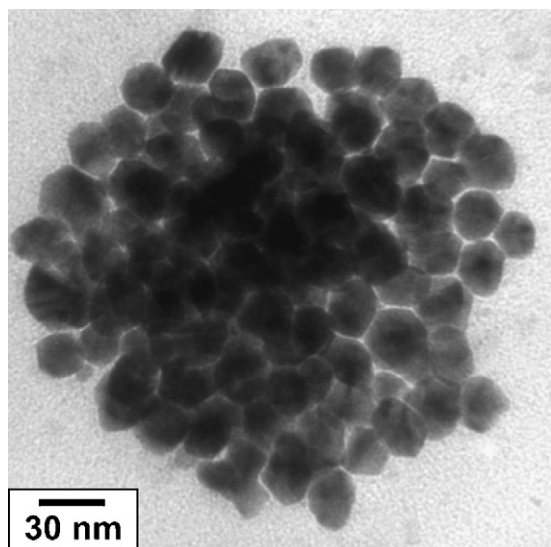


Fig. 8. TEM micrograph of nanoparticles synthesized in toluene.

Table 2 shows the metal distribution coefficient after contacting with toluene. A D -value of more than 100 means that the metal ion of more than 99 wt.% was extracted into the organic solution. As the ratio of AS:OE was changed from 2:1 to 1:2, the D_{Au} -value increased from 87.182 to 247.718 whilst those of other metals were kept in a low level. The absolute amounts of the extracted metals could be obtained from the concentrations in the aqueous solution before and after the extraction, which were about 2 mg zinc and 57 mg gold in the AS/OE ratio of 1/1. That is, from the total 59 mg gold which was initially added, 57 mg gold could be recovered with a purity of about 96 wt.%

The extracted gold was converted to nanoparticles with dodecanethiol and sodium borohydride. Fig. 8 is a TEM micrograph of the product which was formed in the organic solution. The shape and size was uniformly roundish with diameters about 20 nm. The EDS analysis showed that the particles consist of pure gold. Nearest-neighbor lattice spacing was calculated as 0.288 by the average value of 20 atomic lines, which was confirmed as a gold (111) lattice [17]. In addition, the SAED diffractogram in Fig. 9 was also

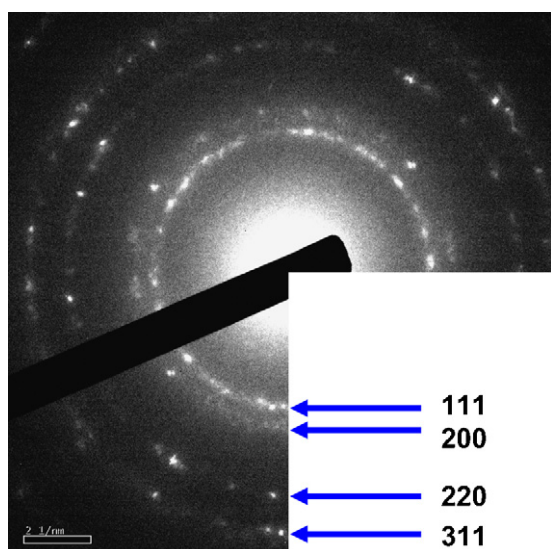


Fig. 9. SAED diffractogram of the nanoparticles observed in Fig. 8.

matched exactly with that of gold reported by Yasuda and Mori [17]. All analyses prove that the product is pure gold nanoparticles in the metal basis.

As stated above, the precious metals from PCB could be recovered with high purity. Especially, the recovered gold nanoparticles could find a wide range of application such as catalysis and sensors. Our last step suggested in Fig. 1 is related to the nickel–zinc separation and will be reported in a separate paper [18].

4. Conclusions

Waste printed circuit boards contain a lot of valuable materials such as gold, silver, and palladium. In this research, we focused on the recovery of the precious metals with high purity. Aqua regia was used as a leachant and the ratio between metals and leachant was fixed at 1/20 (g/ml). Silver is relatively stable in aqua regia so the amount of about 98 wt.% of the input was recovered without an additional treatment. Palladium formed a red precipitate during dissolution, which were consisted of $Pd(NH_4)_2Cl_6$. The amount precipitated was 93 wt.% of the input palladium. In case of gold, a liquid–liquid extraction with toluene was used for a selective extraction. Also, 97 wt.% of the input gold was recovered as nanoparticles by using dodecanethiol and sodium borohydride. The shape and size of the recovered gold nanoparticles was uniformly roundish with diameters about 20 nm.

Aqua regia is a very effective leachant because it makes it possible to separate silver, palladium, and gold at the same time. In addition, the purities of the recovered precious metals were more than 96 wt.%. Therefore, this study could be a promising method to recover precious metals from wastes selectively.

Acknowledgement

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD); KRF-2006-352-D00131

References

- [1] H. Fauve-Buresi, Challenging year for the ICT industry for WEEE and RoHS, in: Proceedings of the 5th International Electronics Recycling Congress, Hamburg, Germany, 2006.
- [2] Europa, Waste Electrical and Electronic Equipment, 2008. http://ec.europa.eu/environment/waste/weee/index_en.htm.
- [3] M. Goosey, R. Kellner, End-of Life Printed Circuit Boards, 2002. <http://www.cfsd.org.uk/seeba/TD/reports/PCB.Study.pdf>.
- [4] S. Zhang, E. Forssberg, Mechanical separation-oriented characterization of electronic scrap, *Resour. Conserv. Recycl.* 21 (1997) 247–269.
- [5] S. Zhang, E. Forssberg, B. Arvidson, W. Moss, Aluminum recovery from electronic scrap by high-force eddy-current separators, *Resour. Conserv. Recycl.* 23 (1998) 225–241.
- [6] W.J. Hall, P.T. Williams, Separation and recovery of materials from scrap printed circuit boards, *Resour. Conserv. Recycl.* 51 (2007) 691–709.
- [7] K. Gloe, P. Mühl, M. Knothe, Recovery of precious metals from electronic scrap, in particular from waste products of the thick-layer technique, *Hydrometallurgy* 25 (1990) 99–110.
- [8] T. Oishi, K. Koyama, H. Konishi, M. Tanaka, J.C. Lee, Influence of ammonium salt on electrowinning of copper from ammoniacal alkaline solutions, *Electrochim. Acta* 53 (2006) 127–132.
- [9] D. Pilone, G.H. Kelsall, Prediction and measurement of multi-metal electrodeposition rates and efficiencies in aqueous acidic chloride media, *Electrochim. Acta* 51 (2006) 3802–3808.
- [10] R.W. Gibson, D.J. Fray, J.G. Sunderland, I.M. Dalrymple, Recovery of solder and electronic components from printed circuit boards, *Electrochim. Soc. P* 18 (2003) 346–354.
- [11] Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., John Wiley & Sons, New York, 1998.
- [12] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid–liquid system, *J. Chem. Soc., Chem. Commun.* (1994) 801–802.
- [13] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 1999, pp. 1001–1014.
- [14] W.C. Moore, Aqua regia, *J. Am. Chem. Soc.* 33 (1911) 1091–1099.

- [15] S. Akita, L. Yang, H. Takeuchi, Solvent extraction of gold(III) from hydrochloric acid media by nonionic surfactants, *Hydrometallurgy* 43 (1996) 37–46.
- [16] N.H. Chung, M. Tabata, Selective extraction of gold(III) in the presence of Pd(II) and Pt(IV) by salting-out of the mixture of 2-propanol and water, *Talanta* 58 (2002) 927–933.
- [17] H. Yasuda, H. Mori, Spontaneous alloying of gold clusters into nanometer-sized antimony clusters, *Z. Phys. D* 40 (1997) 140–143.
- [18] Y.J. Park, D.J. Fray, Separation of zinc and nickel ions in a strong acid through liquid–liquid extraction, *J. Hazard. Mater.* 163 (2009) 259–265.